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Investigating drying behavior of cement mortar through electrochemical impedance spectroscopy analysis

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HIGHLIGHTS

- An EIS method was proposed to evaluate the drying profile of cementitious system.
- The proposed k-n model considered resistivity change along drying direction.
- The proposed model fitted well with the measured spectra of mortars.

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ABSTRACT

In this research, electrochemical impedance measurements were taken on cement mortar with different levels of drying. The impedance spectrum was analyzed with equivalent circuit model, through which the drying behavior was investigated. A model considering resistivity distribution along the drying direction was proposed. For drying of mortar, two different schemes (direct drying and ethanol-pretreated drying) were adopted. Moreover, the influence of hydration time of mortar on drying was also evaluated. Test results showed that the proposed model fitted well with both symmetric and asymmetric spectra for different levels of drying. For cement mortar directly dried at 50 °C for different durations (1, 4, 24, and 48 h), the peak resistivity and drying depth increased with drying time. The ethanol-pretreated mortar showed similar behavior. Moreover, the hydration time of cement mortar was another important factor to influence the drying depth. The proposed model for electrochemical impedance spectrum interpretation provides a low-cost and effective non-destructive approach for understanding the drying behavior of cementitious system.

1. Introduction

Cementitious material (such as concrete and mortar) is the most widely used man-made building material in the world, owing to its versatility and relatively low cost. Most of the time, the on-service concrete and mortars such as in pavement or wall structure applications are subjected to dry conditions from external environment. The removal of water from pores of cement matrix has an essential impact on durability properties [1–4]. For example, it may result in cracking due to tensile stresses induced by drying shrinkage [5,6]. Moreover, it is known that cracks in the matrix fundamentally increase the permeability of the material [7,8]. Therefore, the understanding of drying behavior in cement based materials is essential for understanding their durability.

Various methods have been developed to assess the drying behavior of cement composites caused by moisture distribution. Wei et al. measured the humidity distribution along the depth direction of slab by locating the humidity sensors at different depths [9]. The development of neutron radiography [10,11] and nuclear magnetic resonance techniques [12,13] made it possible to non-destructively detect the drying behavior inside concrete or cement mortar (paste). However, researchers are still seeking for more economical and effective methods to characterize the drying profiles inside cementitious materials.

Recently, electrochemical impedance spectroscopy (EIS) as a non-destructive detecting method has attracted a wider audience. In civil engineering field, EIS was mainly used to evaluate the corrosion behavior of reinforcement [14,15], carbonation of

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concrete [16–18] and ions transformation in cementitious materials [19,20]. Some researchers have also used this technique to study the drying behavior of cement matrix. For example, Beaudoin et al. [1] presented the impedance spectra of cement paste under different levels of drying. However, for the impedance spectra, quantitative analysis was not performed. Sánchez et al. [2] used equivalent circuit to fit the impedance spectra of drying concrete. However, the moisture distribution profile was not given since the concrete was considered as a whole entity. Hence, as per author's knowledge, EIS has not been used to evaluate the drying profile inside the cement matrix.

In this research, the drying behavior of cement mortar was studied by analyzing impedance spectra. The resistivity change due to the moisture distribution was considered. For drying of mortar, two different schemes (direct drying and ethanol-pretreated drying) were adopted. Moreover, the influence of hydration time of mortar on drying was also evaluated. This method provides a low-cost and effective approach for understanding the drying behavior inside cementitious materials.

2. Experimental details

2.1. Specimen preparation and EIS measurement

For the preparation of cement mortar, ordinary Portland cement having strength grade of 42.5 was purchased from Huarun cement plant (Guangdong, China) while standard quartz sand (China ISO Standard Sand Co., Ltd., Xiamen, China) having fineness modulus of 3.02 and specific gravity of 2.61 was used as fine aggregate. EIS measurements were taken on cement mortars having dimensions of $30 * 30 * 30\ mm^3$, water-to-cement ratio of 0.4, and cement-to-sand ratio of 1:1. The specimens were cured for 28 days at room temperature (20 ± 2 °C) and 95% relative humidity. After curing, four sides of specimens were sealed with wax (melting temperature of over 60 °C), leaving two opposite sides open to drying. Thereafter, the specimens were put into an oven operated at 50 °C for different drying time and tested for EIS so as to obtain impedance spectra.

The schematic of two-electrode arrangement for EIS measurement is shown in Fig. 1. It consists of mortar sample, filter paper ($30 * 30\ mm^2$), and steel plate. The filter paper (soaked with 1 ml saturated $Ca(OH)_2$ solution) was applied to unsealed ends of the mortar specimen and was sandwiched between the steel plate and the mortar specimen. EIS measurements were taken on Potentiostat/Galvanostat 283 (Princeton Applied Research Co., PAR, Oak Ridge, TN, USA) with a frequency range of 0.01 Hz–1 MHz.

2.2. Drying methods

In this research, two different schemes were adopted. In the first scheme (direct drying method), the cured samples were waxed and put in oven operation at 50 °C for 1, 4, 24, and 48 h respectively. EIS measurements were then taken on these samples for obtaining impedance spectra. In the second scheme (ethanol-pretreated method), the cured samples were soaked in ethanol for 24 h. After that, the ethanol was refreshed and the samples were allowed to soak for another 24 h. Finally, the samples were waxed and oven dried at 50 °C for 1, 4, 24, and 48 h respectively for EIS measurement.

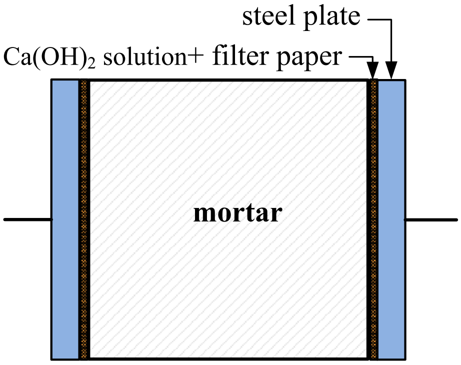

Fig. 1. Schematic view of two-electrode arrangement for EIS measurement.

In order to evaluate the influence of hydration time of cement mortar, the specimens were cured at room temperature (20 ± 2 °C) and 95% relative humidity for 7, 14, and 28 days respectively. At the end of curing period, the specimens were taken out, waxed, and dried at 50 °C for 1 h before conducting EIS measurements.

3. Modeling

The analysis of cement mortar through EIS is based on the electrical characteristics of its components, where an-hydrated and hydrated cement solid and aggregate are considered electrically isolated. Hence, the only conducting path is through the pore solution in capillary and gel pores [21–24]. Traditionally, cement mortar is considered an electrically uniform system and an equivalent circuit (Fig. 2(a)) is usually used to analyze the impedance spectrum [3,25], where R_0, R_1, and C_1 represent high frequency resistance, solid-liquid interface and capacitance of bulk cement mortar while R_{ct} and C_{dl} represent cement-electrode interface charge transfer resistance and double layer capacitance. Most of the time and as reported in literature, R_0 is supposed to be zero or close to zero [25]. Thus, it can be neglected. In Nyquist plot, R_{ct} and C_{dl} represent electrode effect corresponding to Low frequency arc or line (R_{ct} is high enough) and for cement mortar, this part can also be neglected. Consequently, the equivalent circuit in Fig. 2(a) can be represented by simplified circuit (Fig. 2(b)) with impedance

$$Z(\omega) = \frac{R_1}{1 + j\omega C_1 R_1}. \tag{1}$$

However, in some cases, the electrical property of cement mortar is not uniformly distributed. For example, when the cement mortar sample dries from outer surface to inside, the bulk resistance of cement mortar actually varies along drying path due to the evaporation of pore solution. Thus, the impedance of bulk cement mortar can be expressed as

$$Z(\omega) = \sum_{i=1}^{n} \frac{R_i}{1 + j\omega C R_i}. \tag{2}$$

When the pores are saturated, the high frequency capacitance remains constant [4] and hence the value of capacitance was set constant so as to reduce the calculation complexity.

3.1. Resistivity distribution along drying direction

For the cement mortar being dried from outer surface to inside, the variation of resistance along drying direction is caused essentially by resistivity. Under this condition, the resistivity should satisfy the following conditions. As shown in Fig. 3, at the surface where drying depth $t = 0$ (point E in Fig. 3), the surface resistivity ρ_0 is maximum in the entire specimen. The resistivity decreases along drying direction (EBC in Fig. 3) until $t = t_2$ from where the resistivity reaches ρ_δ. This value represents the resistivity of the part of bulk cement mortar not influenced by drying (CD in Fig. 3), and thereafter remains constant (ρ_δ). The distribution of resistivity follows a power-law profile [26,27], i.e., $\rho(t)/\rho_\delta = (t/t_2)^{-\gamma}$, where γ is a constant indicating how sharply the resistivity